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# Functionalised Copper Nanoparticle Catalysts for Electroless Copper Plating on Textiles

Golnaz Taghavi Pourian Azar[1], Daryl Fox[1], Yirij Fedutik[2], Latha Krishnan[1], Andrew J Cobley[1]

[1]Coventry University, The Functional Materials Research Group, Department of Engineering, Environment and Computing, CV1 5FB, Coventry, United Kingdom

[2] Plasmachem GmbH, 12489 Berlin, Germany

## Abstract

Electroless copper plating can be regarded as an enabling technology for electronic textiles, however, the choice of catalyst is critical. In this study, electroless copper plating of a polyester textile was performed using catalysts including a palladium/tin colloid and catalysts based on silver and copper nanoparticles (CuNPs). These CuNPs were functionalised using different ligands including (3-Aminopropyl)triethoxysilane (APTS), oleic acid (OA) and polyacrylic acid (PAA). The catalysts were characterised using Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS) and X-ray Photoelectron Spectroscopy (XPS). The efficacy of different catalysts was determined by characterising electroless copper plated textiles in terms of mass gain (after plating), the coatings coverage and deposits morphology using Scanning Electron Microscopy (SEM). In addition, the sheet resistance of the plated textiles was measured using a four-point probe. The results revealed the important role of functionalising molecules on the performance of CuNPs as a catalyst. The overall best performing CuNP catalyst was CuNP-PAA which had Cu (I) species and the most dispersed and smallest particles. The amount of Cu (I) present in the catalyst, although low (1.7 at. %) seemed critical to the catalyst's efficacy and its ability to produce a smooth and complete electroless copper coating with a very high conductivity.

## Keywords

Electroless copper plating; copper nanoparticle; catalyst; functionalization; textile

## 1. Introduction

Electronic textiles (e-textiles) is an exciting, new field of technology investigating the integration of functional materials with ordinary clothing to produce devices including sensors, energy harvesters, antennas, advanced textiles, and fashion applications. It is an evolving technological platform which is garnering great interest for wearable technology by embedding electronics into textiles to provide the desired functionality for a given application [1], [2], [3].

To achieve high electrical conductivity of metal tracks, approaches such as blending of metal wires are used during yarn formation. However, this method leads to limited flexibility and breaking during manufacturing or after washing and general wear as well as poor comfort levels for the desired wearable applications [4], [5], [6]. Conductive textiles can also be created by coating a non-conductive textile with a layer of conductive material. This can be achieved using coating processes including spraying, electroless plating, sputter coating, plasma treatment, vacuum metallisation, in situ polymerisation and chemical vapour deposition amongst others. Electroless plating has emerged as a process with several advantages for the metallisation of textiles because of its industrial feasibility, low cost, deposit uniformity and high conductivity, as well as ability to create complex patterns and coat a wide range of materials. In addition, the process operates at a relatively low temperature and can be carried out at any stages of the manufacturing process required– thread, roll or garment with no need for a vacuum which is the case for sputter coating [4], [7], [8], [9], [10]. Using electroless copper plating, a selectively coated pattern can be created and used as an electronic circuit, pressure sensor, hydration sensor, heartbeat monitor, temperature, gait analysis and posture for materials such as clothing, furniture and footwear [4], [11]. Key parameters for wearable applications are flexibility, durability, weight and cost without changing the feel or texture of the textile [4], [6], [8], [12]. The scale-up of the

experimental procedure is therefore an important consideration to produce complex electronic architectures on textiles [13]. Subtractive techniques such as etching and scouring in addition to the sensitisation, rinsing and activation steps which add complexity and cost in production of the coating should be avoided [4], [13].

Electroless copper plating is an extensively applied technique which is particularly useful when coating insulating materials such as the dielectric substrates of Printed Circuit Board (PCB) [11], textiles [4] and glass [14], [15]. Electroless copper plating of non-conductive materials such as textiles requires the use of a catalyst which is coated onto the surface of the substrate. This catalyst initiates a redox reaction which allows copper to be reduced from ions in electrolyte at a regular rate with formaldehyde as a reducing agent, resulting in a uniform metallic coating. Subsequent copper plating is then catalysed by the deposited copper coating and hence the process is often described as auto-catalytic [4], [11]. Obtaining a uniform copper deposit is heavily dependent upon the efficacy of the catalyst. Palladium/tin colloid is by far the most widely used catalyst to activate the electroless plating quickly [6], [13]. However, with the increasing cost and lower supply of palladium [8], [16] as well as its presence on the critical raw materials list in Europe, palladium-free (Pd-free) catalysts are desirable [17]. Silver and copper are alternative candidates as catalysts for electroless plating; though copper is more favourable due to being earth abundant, its stability and significantly lower cost [8], [11], [13], [15], [16].

Electroless copper catalysts based on copper nanoparticles (CuNPs) have been prepared by dispersing them in a liquid medium by ultrasonication at low frequency to form a stable, homogenous, low % weight volume CuNP dispersion [16], [18]. Ultrasonication is applied to break down agglomerated CuNPs by inducing acoustic cavitation [19]. Though bare copper is a less active catalyst than palladium and silver, its performance can be improved by the use of different ligands. Ligands are organic molecules which stabilise or functionalise CuNPs and attach them to the material to facilitate the electroless copper plating.

A functionalised nanoparticle (NP) catalyst often uses two functional groups, one at the head and the other one at the tail [13], such as carboxylic acid, methyl or amine groups. The functional group at the tail of the molecule attaches to the NP and the head group attaches to the substrate when in the catalyst dispersion [6]. Through wide studies in the literature for this type of functionalisation [13], [20], many approaches have been adopted for the preparation of NPs and their functionalisation. A range of molecules including adipic acid, silanes and octadecanethiol have been studied to functionalise CuNPs [13]. The functionalised CuNPs have then been applied as catalysts for electroless copper plating of both smooth and roughened PCB surfaces and each molecule was found to possess a different tendency to attach to the CuNPs and/or the substrate [13].

For textiles, studies have investigated the use of Pd-free catalysts for electroless copper plating. It has been shown by Wills et al [4] that textiles can be coated with a silver nanoparticle (AgNP) catalyst through spraying and printing techniques. They found that cotton was successfully plated with electroless copper to produce a conductive glove with sheet resistance values of typically ≤2 Ω/sq. Ali et al [8] activated the surface of cotton textiles by deposition of CuNPs and AgNPs by sequentially dipping in solutions of metal salts and reducing agents before electroless copper plating, resulting in the surface resistivity values of around 20 Ω. Root et al [21] used electroless copper deposition to plate woven cellulose textiles via surface activation through the insertion of silver and tin ions. The range of electrical sheet resistance values recorded were between 16.5 and 369.3 Ω/sq, indicating a non-homogenous deposition of the metal across the substrate [21]. However, to the knowledge of the authors, there is no study on the functionalisation of CuNPs with different ligands and their application as a catalyst for electroless copper plating of textiles.

This paper aims to investigate the effect of different CuNP-based catalysts on the electroless copper plating of textiles and compare their performance with Pd- and Ag-based catalysts. A selection of functionalised CuNP catalysts have been produced using various functionalising

molecules including (3-Aminopropyl)triethoxysilane (APTS), oleic acid (OA) and polyacrylic acid (PAA) through ultrasonication creating dispersions of NPs in the solvent used. The functionalised CuNPs have then been employed and compared to palladium/tin colloidal and AgNP catalysts in terms of their ability to produce a uniform, conductive coating of copper onto the textile. The characterisation of each catalyst and copper plated textiles was conducted using Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), X-Ray Photoelectron Spectroscopy (XPS), mass gain measurements, Scanning Electron Microscopy (SEM) and sheet resistance measurements using a four-point probe.

## 2. Experimental

### 2.1. Materials

A sheet of Polyester Crepe de Chine White was obtained from Whaley's Bradford and sectioned into samples with area of 6.25 $cm^2$. The chemicals for the standard electroless copper plating process (using Pd/Sn colloidal catalyst) were obtained from A-Gas Electronic Materials, including Circuposit Conditioner 3320A, Circuposit Pre-dip 3340, Circuposit Catalyst 3344 and Circuposit 3350-1. The electroless copper electrolyte was made up according to the supplier data sheets. Sodium hydroxide (≥98%, Honeywell), silver nitrate (ACS, >99.9% metals basis, Alfa Aesar) and sodium borohydride (99%, powder, ACROS Organics) required for the synthesis of AgNPs, in addition to (3-Aminopropyl)triethoxysilane (APTS) (97%, Sigma-Aldrich) and isopropanol (Extra Pure, SLR, Fisher Chemical) for preparation of CuNP-APTS catalyst, were all purchased from Fischer Scientific. Commercial copper nanopowders (Cu, 99.8%, primary particle size 25 nm) were supplied from SkySpring Nanomaterials in dry powder form in sealed pouches and used to synthesise CuNP-APTS catalyst. The chemicals for preparation of CuNP-OA and CuNP-PAA colloids were purchased from Sigma-Aldrich, including copper (II) acetate monohydrate (98%), poly(acrylic acid, sodium salt) solution (average $M_w$ ~8000, 45 wt. % in $H_2O$), hydrazine (64-65%, reagent

grade, 98%) and oleic acid (technical grade, 90%). An ammonia solution (30 % ROTIPURAN®) was obtained from Carl Roth.

### 2.2. Equipment

Ultrasonication was performed using a Sonic and Materials Inc. probe, Model VC 750. The instrument generated 20 kHz ultrasound with a maximum power output of 750 W. An ultrasonic horn with a tip diameter of 1.3 cm was attached to the probe which transferred the high frequency voltage output into mechanical vibrations using piezoelectric transducers. The ultrasonic probe was calibrated using the calorimetry method [22] for 100 ml of dispersion. An ice bath was used to keep the temperature of the dispersions below 50 $^{o}$C during ultrasonication.

### 2.3. Electroless copper plating procedure using Pd/Sn colloidal catalyst

The electroless copper plating procedure using a Pd/Sn colloidal catalyst is illustrated in Fig. 1. The 6$^{th}$ and 7$^{th}$ steps shown were used for all other catalysts (AgNP and CuNP catalysts). This approach was used as a standard procedure through which electroless copper plating of textiles was achieved. The optimum electroless plating time for the standard electroless copper plating process (using a Pd/Sn colloidal catalyst) was determined as 25 min by the supplier. The reason is that the concentration of additives in the electrolyte will drop during the plating time and any plating time beyond 25 min will lead to a deterioration in the plating quality. In order to be able to compare the other catalysts with the Pd/Sn colloidal catalyst, the plating time was therefore kept consistent as 25 min for all of them.

### 2.4. Electroless copper plating procedure using AgNP catalyst

The AgNP catalyst preparation method was developed and described by Wills et al. [4]. A solution of 1.639 mM sodium borohydride was made up in 0.1 M NaOH and sprayed onto the textile before a solution of 25 mM silver nitrate made up in deionised water was sprayed onto

the surface. AgNPs were formed immediately in situ on the textile. The sample was then dried in an oven at 65 ºC for 15 min before the spraying and drying steps were repeated two more times. The resulting AgNP catalysed textile was rinsed under running water and went through the 6$^{th}$ and 7$^{th}$ steps shown in Fig. 1.

### 2.5. Electroless copper plating procedure using CuNP catalysts

#### 2.5.1. Preparation of CuNP-APTS catalyst

As the first ligand, (3-Aminopropyl)triethoxysilane (APTS) was selected to functionalise CuNPs in order to catalyse the metallisation of textiles using electroless copper plating. The method described by Litchfield et al. [13] was followed for producing CuNP-APTS catalyst, although this method had not been tested on textiles before. Commercial bare copper nanopowders were weighed accurately to make a 0.1 % w/v mixture in 5 mM APTS made up in isopropanol. The CuNPs were dispersed using an ultrasonic probe at 20 kHz and 81 W/100 ml for 30 min and then centrifuged at 4600 rpm for 2 h. The ultrasonication and centrifuge steps were repeated in isopropanol, followed by a final re-dispersion by ultrasonication in fresh isopropanol. After going through the 1$^{st}$ and 2$^{nd}$ steps illustrated in Fig. 1, the textile sample was immersed in the dispersed CuNP-APTS catalyst at 40 ºC for 30 min followed by 6$^{th}$ and 7$^{th}$ steps (Fig. 1).

#### 2.5.2. Synthesis of CuNP-OA and CuNP-PAA colloids

An aqueous solution containing copper-ammonia complex and copper (II) hydroxide as the copper species was used to synthesise CuNPs according to the following procedure: 20 g of copper (II) acetate monohydrate was dissolved in 15 ml of 28 wt. % aqueous ammonia and 50 ml of water to form a royal blue solution. The required amount of 15 M sodium hydroxide solution was then added to form the desired ratio of the precursor. Subsequently, the reaction mixture was heated to 50 °C. The aqueous hydrazine solution was added to the reaction

medium while stirring vigorously in an inert atmosphere for 15-20 min. The reagent used was $Cu^{2+}/NH_3/NaOH/N_2H_4$: 1/2/0.5/4.

During the synthesis, CuNPs were well-dispersed in the reaction medium without any agglomeration due to stabilisation by ammonium and acetate ions. In order to modify the particles, it is necessary to replace ammonium and acetate ions with passivating agents. After hydrazine reduction, the particles surface can be modified by adding in the passivating agents to the reaction mixture. In order to functionalise CuNPs, a solution of oleic acid (OA) (5% solution of OA in ethanol) or polyacrylic acid (PAA) was added to the CuNPs under gentle mixing and then an equal amount of ethanol was added to this reaction mixture. The mixture was stirred vigorously for 1 h under an inert atmosphere. The particles were separated from the solution and washed a few times by dissolution in toluene for OA or water for PAA and precipitated by ethanol. The CuNPs were then re-dispersed in isopropanol for OA or water for PAA by sonication in an ultrasonic bath (44.8 kHz, 60 W/1 l) for 1 h. The concentration of the stabilised CuNPs in the final colloids was determined by gravimetric analysis and colloids diluted to 0.1 and 3.5 wt./v. % for CuNP-OA and CuNP-PAA, respectively.

### 2.5.3. Preparation of CuNP-OA and CuNP-PAA catalysts

To prepare the catalysts, 100 ml of the prepared mixtures (see section 2.5.2) was re-dispersed using an ultrasonic probe at 20 kHz and 81 W/100 ml for 30 min. After going through the 1$^{st}$ and 2$^{nd}$ steps shown in Fig. 1, the textile samples were immersed in the catalyst dispersions for 30 min at 40 $^{o}$C followed by 6$^{th}$ and 7$^{th}$ steps (Fig. 1).

## 2.6. Characterisation of the samples

Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) techniques were used to determine the particle size of various catalysts. Samples for TEM analysis were prepared by pipetting a few drops of the dispersed catalyst onto a holey carbon film on a 200 mesh copper grid placed on top of a filter paper. The grids were air dried overnight and then

placed in the TEM system (FEI Talos F200X) which was equipped with a super X EDS. The system was operated at 200 kV and data was acquired using Velox software. As AgNPs were synthesised in situ on the textile substrate and, in this case, the substrate has an effect on the properties of synthesised NPs, it was not possible to perform TEM analysis on AgNP catalyst. For DLS analysis, a Zetasizer Nano ZS instrument (Malvern Instruments) with a Zetasizer software was used at 25 °C on the different CuNP catalyst dispersions. The refractive index was set at 1.330 for aqueous dispersants and 1.39 for isopropanol. A sample of 2 ml of each dispersion was added to a disposable cell and the analysis was repeated five times for each sample after an equilibration time of 180 seconds. X-ray Photoelectron Spectroscopy (XPS) (Thermofisher ESCALAB 250) equipped with Al Kα X-ray source was used in order to assess the composition and chemical state of the surface elements on the textiles coated with Pd/Sn colloidal and different CuNP catalysts (before electroless copper plating). The analysis was also performed on an uncoated textile to determine the peaks which were related to the substrate. Schofield cross sections were used to calculate the relative atomic concentrations from the intensities of the major photoelectron spectral lines by means of codes incorporated in the instrument data system.

The mass gain of the textiles during electroless copper plating was measured to determine the amount of electroless copper deposited for each catalyst. It was calculated by measuring the mass of each sample before and after electroless copper plating and drying at 45 $^{o}$C (typically overnight). The surface morphology of the electroless copper coatings was characterised using Scanning Electron Microscopy (SEM) (ZEISS GEMINI 500 VP). The sheet resistance of the electroless copper plated textiles was measured using a four-point probe (RM3000+ current source and Microposition Probe, Jandel Engineering Limited) at five points for each sample. The constant current applied to the textile samples was 100 mA and the reference measurement was 13.15 Ω/sq at an applied current of 10 mA from a plate of indium oxide. The probe spacing was 1 mm.

## 3. Results and Discussion

Electroless plating electrolytes are designed so that the reduction of the ions and metal deposition do not proceed homogeneously (plating electrolyte is stable) and the metal deposits heterogeneously on the catalytic surface. Electroless copper deposition is a complex process. It is often thought of as being electrochemical in nature whereby the surface at which deposition is occurring (be that the initial catalyst or the deposited metal) is both anodic and cathodic at the same time. Formaldehyde is oxidised at the anodic areas releasing electrons which are then used at the cathodic sites for the reduction of copper ions to copper metal. From the above, it is clear that the particle size of the catalyst (the surface area of the particles), the uniformity of their size, their distribution on the surface (agglomeration behaviour) as well as the surface quality of the particles have a great influence on the extent of the autocatalytic plating reaction.

### 3.1. TEM characterisation of different catalysts

As particle size is one of the most important factors to determine the catalytic activity and performance of catalysts [23], the synthesised catalysts were examined by TEM to analyse their particle sizes and the results are depicted in Fig. 2. The Pd/Sn colloidal catalyst consists of homogeneously distributed well-dispersed sub 20 nm NPs (Fig. 2a) as expected. It was found that both CuNP-APTS and CuNP-OA catalysts are composed of agglomerates of 50 nm and sub 50 nm NPs, as shown in Fig. 2b and 2c, respectively. However, the CuNP agglomerates are larger in CuNP-OA catalyst (Fig. 2c) compared to the ones in CuNP-APTS catalyst (Fig. 2b). By contrast, CuNP-PAA catalyst consists of isolated well-dispersed CuNPs having the sizes of 50 nm and sub 50 nm (Fig. 2d).

### 3.2. DLS analysis of CuNP catalysts

CuNP catalyst dispersions were tested using a DLS nanosizer to verify the presence of large CuNP agglomerates in CuNP-APTS and CuNP-OA catalysts and to confirm that the observed

agglomerates in TEM results were not artifacts formed during the drying of the NPs on the carbon films. The results of these measurements are depicted in Fig. 3.

The measured particle size for CuNP-APTS and CuNP-OA catalysts by DLS was 151 nm and 405 nm, respectively (Fig. 3a & b). These results are in a good agreement with TEM observations (Fig. 2b & c) verifying that the NPs in CuNP-OA catalyst have been in the form of larger agglomerates compared to the ones in CuNP-APTS catalyst. On the other hand, the particle size of CuNP-PAA catalyst was measured to be 53 nm by DLS (Fig. 3c) which is in agreement with TEM observation (Fig. 2d). The results in Fig. 3 show that among the CuNP catalysts, the largest and smallest particles were associated with CuNP-OA and CuNP-PAA catalysts, respectively.

Ligands that are used for stabilising the CuNPs not only influence the catalytic activity by changing the surface quality of the particles but they also have an effect on the stability, particle size and agglomeration behaviour. Since PAA is a multidentate polymeric ligand, it provides stronger interaction with the surface of the particles creating electrostatic and steric stabilisation and leading to smaller particle size. For OA which is a monodentate ligand, the reversible sorption/desorption of the ligand will proceed leading to the lower stability to oxidation and agglomeration (an increased particle size). For APTS, a silica shell is formed which helps to protect the particles against the oxidation but does not provide enough stabilisation from agglomeration.

The surface area of NPs is an important factor in determining their catalytic behaviour. Therefore, in this study, the particle size of the catalysts is expected to exert an important effect on the initiation time of electroless copper plating, and the degree of coverage as well as the conductivity of the subsequent electroless copper coating.

### 3.3. XPS analysis of catalyst coated samples

XPS analysis was conducted on the textile samples coated by the different catalysts and the calculated relative quantities are presented in Table I. In the XPS result for the Pd/Sn colloidal catalyst coated sample, Pd was present in both of its main chemical states, Pd (0) and Pd (II). Metallic palladium– Pd (0) has been more significant in the catalyst layer than Pd (II). The Pd (II) is thought to be due to some residual $PdCl_2$ present in the catalyst dispersion or Pd-N bonding [6]. The energy of the detected Sn peak suggests that this was in the form of Sn (IV), as expected. There were C-N bonds that may come from the components from the pre-dip or conditioner i.e. 2-aminoethanol or polyamine.

Regarding the surface quality of the catalyst particles, CuNPs unlike noble metal catalysts (Au, Ag, Pd, etc.) oxidise easily in the air. The ligands used stabilise two oxidation states in a transition metal redox couple (Cu (I)/Cu (II)) differently so that species with higher or lower oxidation state can be formed on the particles surface. So CuNP catalyst in reality is not in the form of pure CuNPs with pure metallic surface but they exist as kind of a core-shell system consisting of metallic copper core and shell of some density, composition and porosity [24], [25].

In the CuNP-APTS catalyst coated sample, the detected copper was in the form of Cu (II), which is normally characteristic of CuO, although the energy of Cu $2p^3$ peak is a little high for this species.

The chemical structure of an APTS molecule ($NH_2$-$(CH_2)_3$-$Si(OCH_3)_3$) consists of a head group (-$Si(OCH_3)_3$) which is expected to couple to the textile surface. This enables the methylene chains (-$(CH_2)_3$-) to pack together to expose the tail group (-$NH_2$) at the surface. It is these tail group species that are intended to interact with the CuNPs [6] and stabilise Cu (II) on the surface during oxidation. The C-N and Si possibly originate from the stabilising APTS molecule and the level of C-N bonded material was the highest on this sample.

In the CuNP-OA catalyst coated sample, the analysed copper was also in the form of Cu (II). The amount of detected Cu species was the highest in this sample (11.7 at. %-Table I).

OA is a surfactant that has amphiphilic properties with a long hydrocarbon chain as the hydrophobic group and carboxylic acid group as hydrophilic. Surfactants which contain carboxylic acids are used as lubricants, corrosion-resistant materials, and catalysts [26]. The modification mechanism of OA on the surface of NPs can be considered as the co-ordination between the carboxylate ion ($COO^-$) of OA and the surface of NPs, producing a dense protective monolayer that binds firmly to the NPs surface and stabilises Cu (II) on the surface during oxidation [27], [28], [29], [30], [31], [32].

In the CuNP-PAA coated textile, detected copper was in the form of Cu (I), which is characteristic of $Cu_2O$. The amount of detected Cu species was the lowest in this sample (1.7 at. %-Table I). In both of the CuNP-OA and CuNP-PAA coated samples, the C-N bonds present may be residues from the electroless copper pre-treatment process in particular the commercial Conditioner solution which contains 2-Aminoethanol or polyamine.

PAA is a polymer with a 3D network while hydrophilic carboxyl groups on both sides of polymer chains are responsible for its superabsorbent characteristic. PAA molecules can bind the polymer on the surface of NPs and make the modified NPs water-soluble while stabilise Cu (I) on the surface [33], [34], [35].

The key finding of the XPS investigation was the presence of copper as Cu (I) in the CuNP-PAA catalyst coated sample and Cu (II) in CuNP-APTS and CuNP-OA catalyst coated samples. This can be a key characteristic in determining their ability to initiate electroless copper plating in addition to their particle sizes. In the case of the CuNP catalysts, the catalytic activity significantly depends on the various copper species. Metallic copper and copper oxide phases are all important for catalysing several important reactions [36]. The stability of an oxidation state for a copper complex depends on the type of bonding and

geometry of the formed complex. Cu (I) is a soft metal ion and therefore it prefers soft donor sites like sulphur, halides and purines [37]. While Cu (II) is borderline and forms more stable complexes with borderline donors like nitrogen such as the well-known dark blue $[Cu(NH_3)_4]^{2+}$ complex. Cu (I) prefers sp3 hybridise and hence the tetrahedral geometry of the complex is more stable for Cu (I). In contrast, Cu (II) prefers a distorted octahedral geometry. Accordingly, the preferred formation of Cu (I) or Cu (II) on the surface of CuNPs can be observed during oxidation, depending on the used ligand. Prucek et al. [38] have shown that metallic copper particles in the presence of PAA were fully transformed to $Cu_2O$ particles (Cu (I)) due to oxidation in the air, and no formation of Cu (II) has been found, which is in agreement with our findings.

The catalytic activity of Cu (I) oxide has been investigated in the literature. Sasmal et al. [24] found the catalytic activity of $Cu_2O$ to be much higher than that of the metallic CuNPs. They confirmed that the exceptionally high catalytic activity of $Cu_2O$ based NPs over other noble metal NPs for 4-nitrophenol reduction has been due to the in situ generated ternary nanocomposite, $Cu_2O$-Cu-CuO [24]. Pike et al. have also mentioned that $Cu_2O$ has higher catalytic activity in the splitting of water to $O_2$ and $H_2$ and has also a greater catalytic activity than CuO in the oxidation of CO [25].

Fig. 4 depicts the Cu2p spectra for different CuNP catalysts detailing how Cu (I) and Cu (II) peaks were realised by XPS investigation. Fig. 4a shows the presence of Cu (I) in the CuNP-PAA catalyst. The major peak positions of Cu (I) are almost identical to those for Cu (0), but the presence of the weak satellite shows that the spectra are of Cu (I). The two chemical states can further be distinguished by considering the Cu LMM Auger peaks. The Cu (I) Auger line occurs at around 915.5 eV, whereas the Cu (0) LMM Auger peak is at an energy of about 918 eV. An inspection of the survey scan spectra for this sample (Fig. 4d) shows the Cu LMM Auger peak occurs at around 915.5 eV. There was no peak visible at 918 eV. Hence, there was no evidence for metallic Cu in the spectra to the sampling depth of 10 nm. On the other

hand, Fig. 4b and 4c clearly show that Cu was present as Cu (II) in CuNP-APTS and CuNP-OA coated samples. In the Cu2p spectra from these samples, the Cu peaks are approximately 1 eV higher than those for Cu (I), but there is also a significant satellite peak present.

### 3.4. Visual inspection and copper mass gain after electroless plating

The coatings were visually inspected immediately after electroless copper plating. Fig. 5 shows the appearance of the textile samples before and after electroless copper plating using different catalysts. It can be seen that among the electroless copper coatings catalysed by CuNPs, the sample catalysed by CuNP-PAA (Fig. 5f) was the most similar to the coatings catalysed by Pd/Sn colloid (Fig. 5b) and AgNPs (Fig. 5b) with respect to the degree of coverage of the electroless copper coating on the textile. On the other hand, it was observed that the poorest coverage of the textile by the electroless copper process was catalysed by CuNP-APTS (Fig. 5d), followed by the coating catalysed by CuNP-OA (Fig. 5e).

The copper mass gain of the samples after electroless plating using different catalysts was measured to compare the catalysts ability to initiate electroless copper plating. It was observed that the copper mass gain after electroless plating is hugely dependent on the catalyst used (Fig. 6). The mass gains of copper plated textiles initiated by the Pd/Sn colloidal, AgNP and CuNP-OA catalysts were comparable (Fig. 6). Meanwhile, the CuNP-APTS catalysed textile resulted in a much lower mass gain whereas the CuNP-PAA catalysed sample recorded a significantly higher mass gain compared to all other catalysts.

It should be considered that all the deposits being investigated in this study were the same (so the same molecular weight and density) and the surface area of all the textile substrates were exactly the same. Therefore, the amount of metal deposited (electroless copper mass gain) can be a good indicator to compare the average thickness of the coatings. However, it is not enough to precisely evaluate the efficacy of different catalysts since it assumes the coating is

distributed evenly across the substrate. Accordingly, the thickness and evenness of the coatings should be regarded together to evaluate catalysts efficacy.

### 3.5. SEM characterisation of different electroless copper coatings

The SEM characterisation of copper plated textile samples catalysed by Pd/Sn colloid, AgNPs and different CuNPs is illustrated in Fig. 7. These micrographs provide information on the degree of the surface coverage and the morphology of the coatings obtained. SEM images show that the electroless copper coatings covered all fibres completely and consistently when Pd/Sn colloid (Fig. 7a) and AgNPs (Fig. 7b) were used as catalysts. The morphology and uniformity of electroless copper coatings obtained by using Pd/Sn colloidal and AgNP catalysts were subsequently used as a reference for the following CuNP catalysed coatings.

Although both CuNP-APTS and CuNP-OA catalysts consisted of Cu (II) species, their ability to initiate electroless copper plating was very different. The electroless copper plated sample catalysed by CuNP-APTS, when observed visually, appeared to be partially coated (Fig. 5d). However, when a coated part of the sample was investigated under SEM, the result showed a good and nearly uniform coverage of those fibres by the electroless copper coating (Fig. 7c). By contrast, the CuNP-OA catalysed textile was mostly covered by electroless copper coating when visually examined after plating (Fig. 5e). However, it showed an incomplete coverage of the fibres with a non-uniform thickness of the coating and a nodular morphology all over the sample when investigated by SEM (Fig. 7d). The reason for this observation can be due to the different amounts of the catalyst species on the surface combined with the different particle size of these species, originating from the different functionalising molecules. On the CuNP-OA catalysed sample, there was a higher amount of Cu (II) species (11.7 at. %-Table I) in the form of larger agglomerates (Fig. 2c). The higher amount of Cu (II) species resulted in a higher electroless copper mass gain compared to the mass gain for the CuNP-APTS catalysed sample (Fig. 6) and this can be the reason for a more complete coating all over the

textile sample upon visual inspection (Fig. 5d & e). However, the presence of larger agglomerates resulted in the local accumulation of the coating on the micro scale and an incomplete coating with a non-uniform thickness (Fig. 7d). In contrast, the lower amount of Cu (II) species (3.7 at. %-Table I) on a CuNP-APTS catalysed sample had not been sufficient to result in an adequate copper mass gain and a complete coating all over the sample on visual examination (Fig. 5d). It resulted in a lower electroless copper mass gain compared to when a CuNP-OA catalyst was employed (Fig. 6). However, smaller agglomerates of catalyst NPs (Fig. 2b) has provided a smooth and nearly uniform electroless copper coating on the coated parts of the sample (Fig. 7c).

Comparing the copper mass gains and SEM results of electroless copper plated textiles catalysed by CuNP-APTS and CuNP-OA verified that the higher amount of electroless copper deposited is not the only important criterion for the efficacy of a catalyst and it does not necessarily result in a coating with a good coverage. Moreover, it was confirmed that besides the catalytic activity of the various catalyst species, their particle size has a significant role on the surface coverage of the subsequent electroless coating.

SEM micrograph of the electroless copper plated textile catalysed by CuNP-PAA (Fig. 7e), showed a complete and uniform coverage of the fibres by electroless copper coating. The most important reason to distinguish this catalyst from the other CuNP catalysts is the presence of Cu (I) species as fine well-dispersed particles. A very low amount of Cu (I) (1.7 at. %-Table I) with a small particle size (53 nm-Fig. 3c) has been enough to give a very high copper mass gain (Fig. 6) in the form of a smooth and complete coating on the fibres (Fig. 7e).

### 3.6. Sheet resistance measurements of electroless copper plated textiles

A four-point probe instrument was used for measuring the sheet resistance of electroless copper plated textiles. The sheet resistance of the metallised fibres is closely related to the

thickness of the copper coating on one hand and strongly depends on how uniform the coating is across the substrate on the other hand. The deposit has to be evenly distributed at a regular thickness to yield a low sheet resistance which is an absolute necessity for e-Textiles. Therefore, as thickness and evenness of copper coatings are critical factors to determine catalysts performance, sheet resistance is another important indicator to prove the efficacy of the catalysts.

The sheet resistance measurement results for copper plated textile samples catalysed by Pd/Sn colloidal, AgNP and CuNP-PAA catalysts at an applied current of 100 mA are summarised in Fig. 8. The highest sheet resistances were measured for the copper plated samples catalysed by CuNP-APTS and CuNP-OA. The selected points were not conductive at all (with a "contact limit" reading) or they gave a higher sheet resistance in the ohms range (3-17 ohms/sq) to make it impossible to show them in the same plot (Fig. 8). This could be explained by the lack of complete coverage of fibres by electroless copper coatings as observed in the SEM images of these samples (Fig. 7c & d). From the full coverage of the fibres by electroless copper coating (Fig. 7e), it was expected that the lowest sheet resistance was recorded by the copper plated sample catalysed by CuNP-PAA and this was the case. The SEM image obtained from a CuNP-PAA catalysed sample showed how the conductivity can be improved by a better surface coverage of the fibres (Fig. 7e).

Considering the excellent surface coverage and higher conductivity of copper plated sample catalysed by CuNP-PAA, this catalyst is judged to be the best performing CuNP catalyst. The reason for this observation is the presence of Cu (I) species as well-dispersed small particles.

The XPS findings and the particle size analyses of the catalysts in combination with the SEM analysis and conductivity measurements of the electroless copper plated textiles indicate that separate from the catalytic activity, well-dispersed smaller catalyst particles significantly improve the performance of the catalysts. Among the CuNP catalysts tested, CuNP-OA

exhibited the largest particle size, the poorest surface coverage and the highest sheet resistances recorded. On the other hand, the CuNP-PAA catalyst showed the smallest particle size, yielded the smoothest coating with the most complete coverage and the highest conductivity compared to the other CuNP catalysts.

## 4. Conclusion

The results of the study clearly indicated the successful application of CuNPs as a catalyst for electroless copper plating of the textiles. An important finding of the study is the differences observed on the efficacy of CuNP catalysts depending on which functionalising molecule was present. It was observed that CuNPs functionalised with APTS and OA generally resulted in incomplete and non-uniform coatings with high resistivity. However, the electroless copper coating catalysed by CuNP-PAA catalyst had a complete coverage with very high conductivity. The reason is attributed to the presence of Cu (I) species as fine well-dispersed particles in CuNP-PAA catalyst compared to the presence of Cu (II) species as agglomerated particles in CuNP-APTS and CuNP-OA catalysts. Selecting the proper functionalising molecule enables CuNPs to be employed as a more cost-effective catalyst option to produce highly conductive electroless copper coatings on textiles suitable for e-textiles and wearable technology.

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**Table I.** XPS Data for Pd/Sn colloidal and different CuNP catalysts with the main associated peaks recorded. The values in each column relates to the relative quantity (atomic percent).

| **Sample** | **Atomic Percent** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C-O | O-C=O | C-N | Pd (0) | Pd (II) | Cu (I) | Cu (II) | Sn | Si | Cl |
| Uncoated | 10.8 | 7.5 | 1.9 | - | - | - | - | - | 1.2 | 0.7 |
| Pd/Sn Colloid | 6.1 | 4.2 | 1.0 | 2.6 | 1.0 | - | - | 12.2 | - | 0.5 |
| CuNP-APTS | 13.8 | 7.4 | 2.4 | - | - | - | 3.7 | - | 1.1 | - |
| CuNP-OA | 16.6 | 6.2 | 1.1 | - | - | - | 11.7 | - | - | - |
| CuNP-PAA | 12.2 | 7.8 | 1.5 | - | - | 1.7 | - | - | 0.4 | - |

## Figure captions

**Fig. 1.** Schematic illustration of electroless copper plating using a Pd/Sn colloidal catalyst.

**Fig. 2.** TEM images of (a) Pd/Sn colloidal, (b) CuNP-APTS, (c) CuNP-OA and (d) CuNP-PAA catalysts.

**Fig. 3.** DLS graphs showing particle size measurements of (a) CuNP-APTS, (b) CuNP-OA and (c) CuNP-PAA catalysts.

**Fig. 4.** XPS results showing Cu2p spectra of (a) CuNP-PAA, (b) CuNP-APTS, (c) CuNP-OA catalysts and (d) XPS survey scan (kinetic energy) for CuNP-PAA sample.

**Fig. 5.** Photograph images of polyester samples (a) before and (b-f) after electroless copper plating for 25 min using (b) Pd/Sn colloidal, (c) AgNP, (d) CuNP-APTS, (e) CuNP-OA and (f) CuNP-PAA catalysts.

**Fig. 6.** Bar chart comparing the electroless copper plated textiles catalysed by Pd/Sn colloidal, AgNP, CuNP-APTS, CuNP-OA and CuNP-PAA catalysts regarding their mass gain.

**Fig. 7.** SEM images of textile samples after electroless copper plating for 25 min using (a) Pd/Sn colloidal, (b) AgNP, (c) CuNP-APTS, (d) CuNP-OA and (e) CuNP-PAA catalysts.

**Fig. 8.** Four-point probe sheet resistance measurements of copper plated textiles using different catalysts at an applied current of 100 mA.

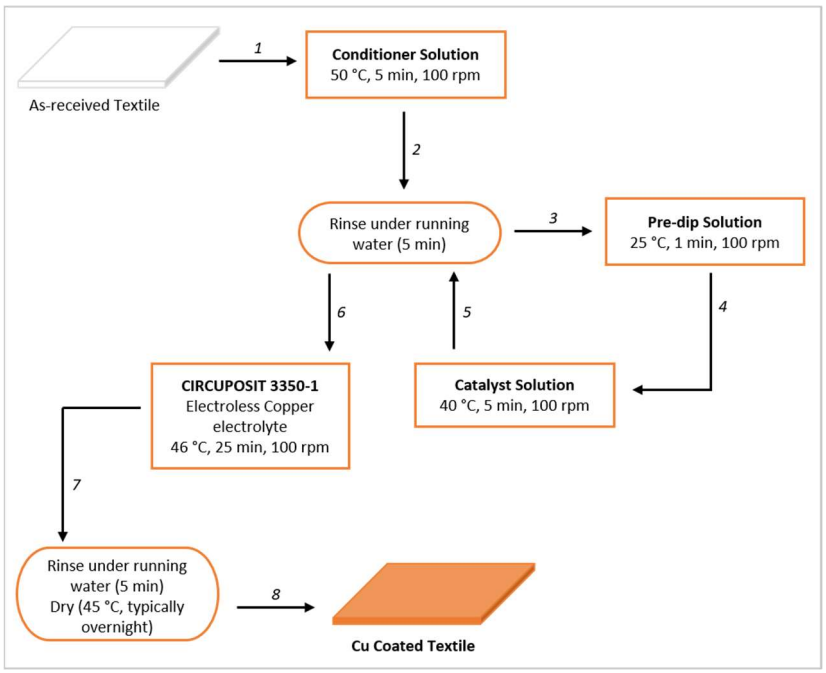
As-received Textile
1
Conditioner Solution
50 °C, 5 min, 100 rpm
2
Rinse under running water (5 min)
3
Pre-dip Solution
25 °C, 1 min, 100 rpm
4
Catalyst Solution
40 °C, 5 min, 100 rpm
5
6
CIRCUPOSIT 3350-1
Electroless Copper electrolyte
46 °C, 25 min, 100 rpm
7
Rinse under running water (5 min)
Dry (45 °C, typically overnight)
8
Cu Coated Textile

Fig. 1

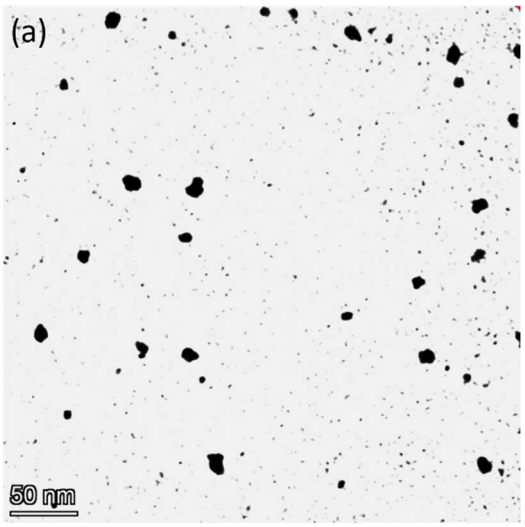

Fig. 2a

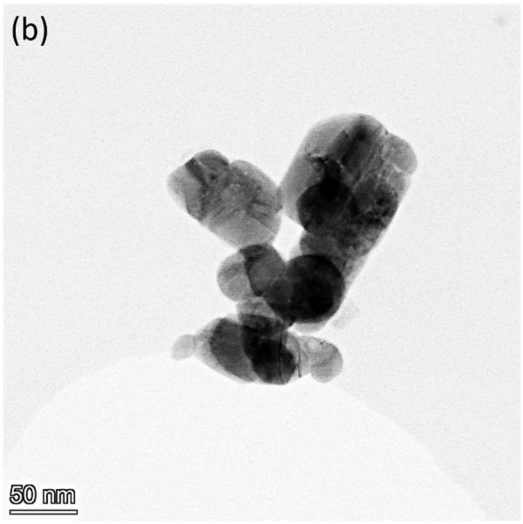

Fig. 2b

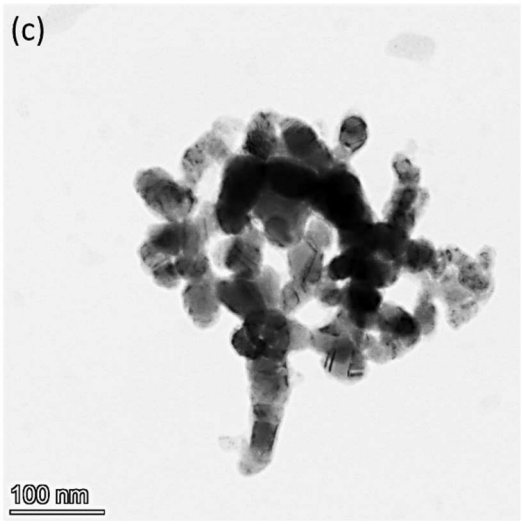

Fig. 2c

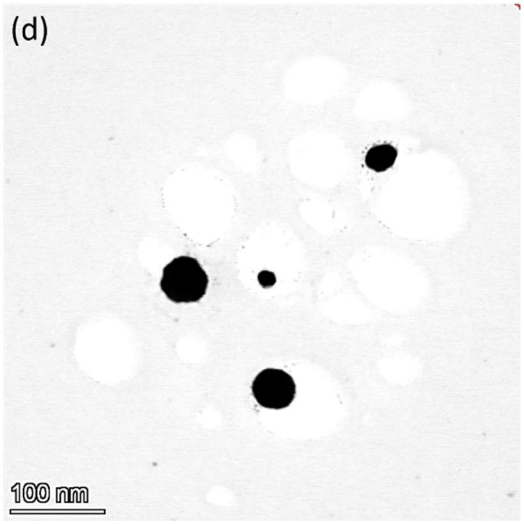

Fig. 2d

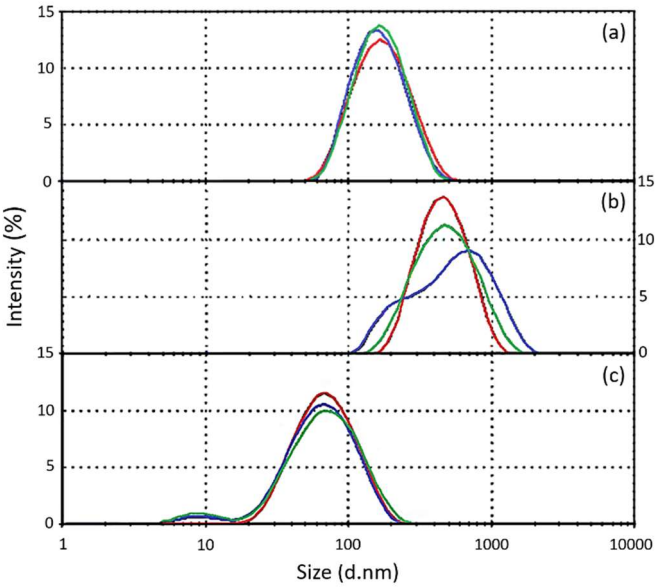


Fig. 3

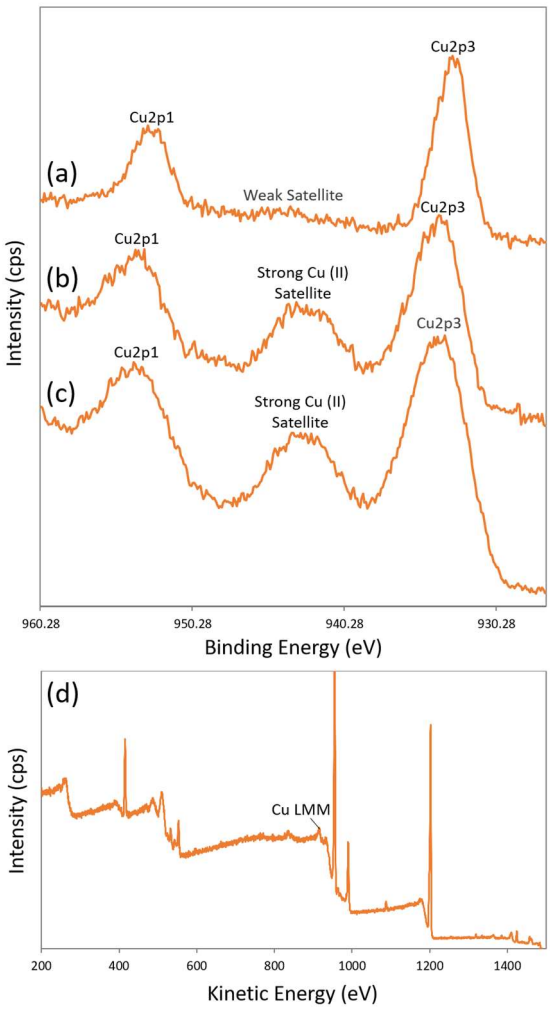
Cu2p3
Cu2p1
(a)
Weak Satellite
Cu2p3
Cu2p1
(b)
Strong Cu (II)
Satellite
Cu2p3
Cu2p1
(c)
Strong Cu (II)
Satellite
Intensity (cps)
960.28
950.28
940.28
930.28
Binding Energy (eV)
(d)
Cu LMM
Intensity (cps)
200
400
600
800
1000
1200
1400
Kinetic Energy (eV)

Fig. 4

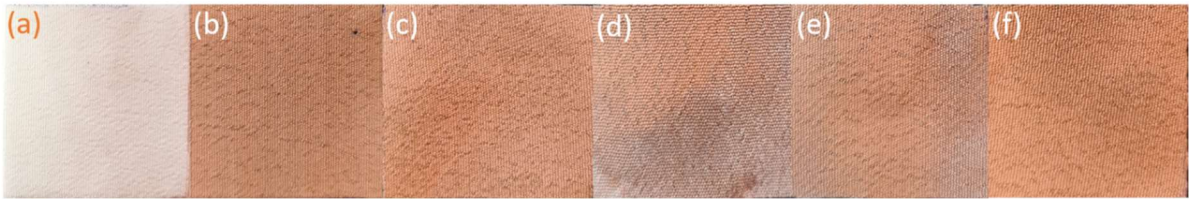

Fig. 5

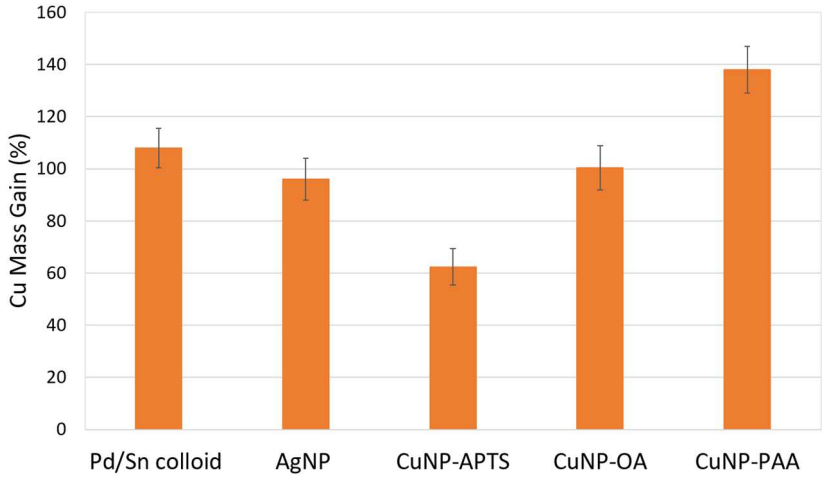
160
140
120
100
80
60
40
20
0
Cu Mass Gain (%)
Pd/Sn colloid
AgNP
CuNP-APTS
CuNP-OA
CuNP-PAA

Fig. 6

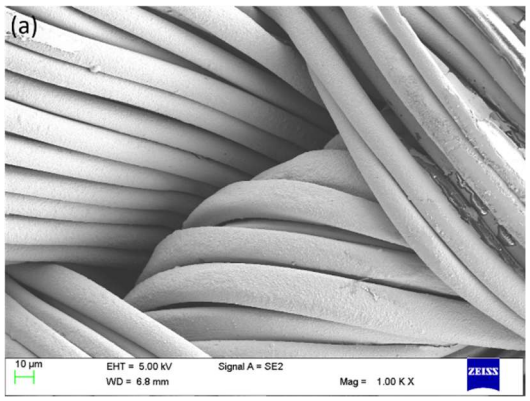

Fig. 7a

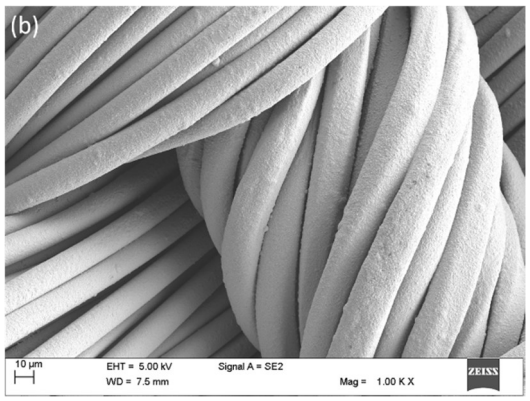

Fig. 7b

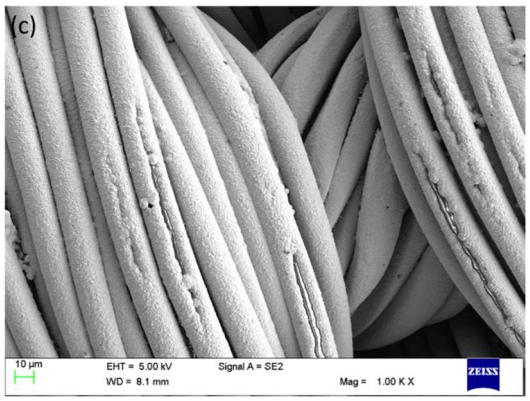

Fig. 7c

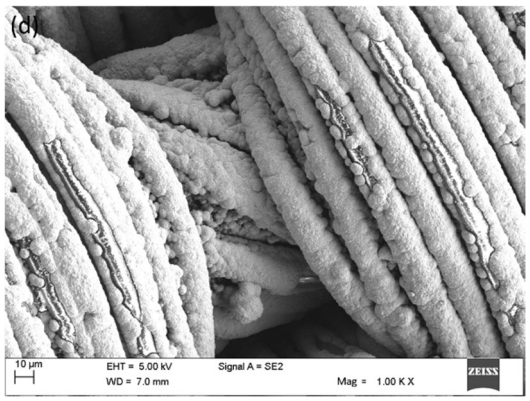

Fig. 7d

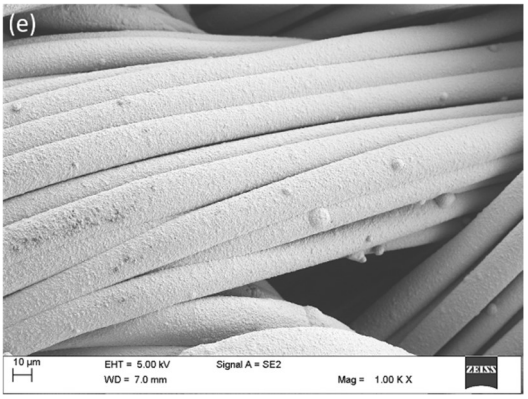

Fig. 7e

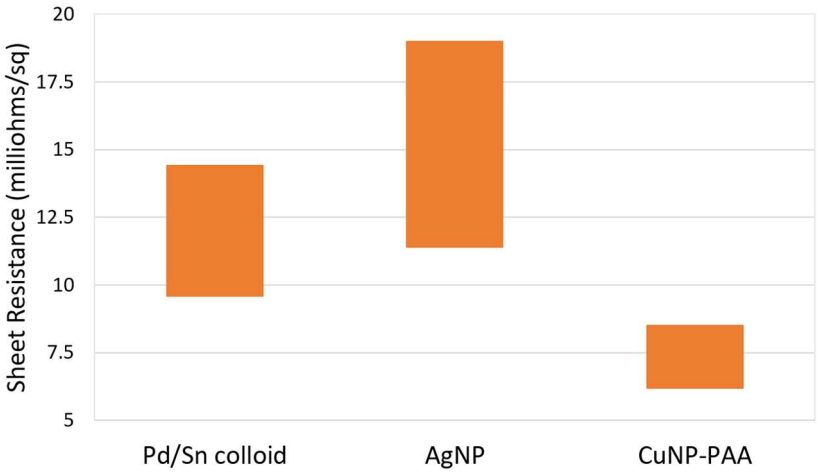
Sheet Resistance (milliohms/sq)
20
17.5
15
12.5
10
7.5
5
Pd/Sn colloid
AgNP
CuNP-PAA

Fig. 8